APPENDIX B

EXAMINATION OF MASS BALANCE ACCOUNTING AS A MEANS FOR ESTIMATING PLUTONIUM RELEASES

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B.1 INTRODUCTION

Citizens interested in release estimates from the Rocky Flats facility have suggested that a mass balance approach should be used to estimate past releases. The idea is to compare the quantity of plutonium brought onsite with the quantity of plutonium leaving the site as a means of estimating past environmental releases of plutonium from the facility.

The idea of using plutonium accountability data to estimate the amount of plutonium released during the 1957 fire was seriously considered at the start of Phase II. In principle, the amount of plutonium that was released in airborne effluent (Q_e, grams [g]) could be estimated if the following were known:

- Plutonium inventory in the affected area prior to the fire (Q_i, g)
- Amounts of plutonium present on the filters prior to the fire (Q_f, g)
- Amount of plutonium recovered after the fire (Q_r, g)
- Amounts of plutonium in liquid and solid wastes generated during cleanup (Q_w, g)
- Residual contamination after cleanup (Q_{rc}, g) that was painted over to prevent resuspension that would produce airborne contamination and expose workers.

In the following equation, the quantities contributing to the pre-fire total are shown on the left side. The post-fire quantities, plus the amount of plutonium in airborne effluent, are shown on the right.

$$Q_i + Q_f = Q_r + Q_w + Q_{rc} + Q_e \qquad \text{(B-1)}$$

This equation can be solved for Q_e, and, if the quantities listed above are known, the release can be calculated using this material balance approach.

There appeared to be a reasonable chance that a mass balance approach could be used for the 1957 fire. First, we noted that the fire was limited to a relatively small area. Second, it was expected that, because of the much higher value of plutonium, the accountability data would be more reliable than data on uranium with which we had previous experience (Voillequé et al. 1995). (Citizens have expressed this same idea: because plutonium was more valuable than gold, you would expect that those responsible would know where every last bit was.) Both these factors favored collecting good information about Q_i and Q_r. In addition, the facility had operated for only a few years, duct and effluent monitoring had been performed, and it was believed that the filters had not been changed. For those reasons, it was expected that a good estimate of Q_f could be made. Estimates of the amounts of plutonium in solid wastes (Q_w) were known to exist, and it was expected that the residual contamination could be estimated from survey data.

The following sections describe the results of our investigation into plutonium accounting at Rocky Flats. Section B.2 describes the data that were found for the major fires (1957 and 1969).

Section B.3 examines the possible utility of the mass balance approach for routine operations. That analysis revealed generic problems associated with the use of mass balance accounting during the early years (before 1970) at Rocky Flats. Section B.4 contains a summary of the results.

B.2 COMPARISON OF RESULTS FOR 1957 AND 1969 FIRES

One of our first goals while searching through the classified records at Rocky Flats was to identify information on plutonium accountability for the September 1957 fire in Room 180 of Building 71 and the May 1969 fire in Buildings 776-777. The search was successful. Records of the plutonium loss for the 1957 fire were found in monthly accountability reports made between the time the fire and completion of the final cleanup of Room 180 several years later. An accounting of the pre- and post-fire inventories of plutonium in Buildings 776-777 was also found in the classified records.

We requested and obtained declassification of notes taken while reviewing the 1957 fire data and of documents containing accountability data for both events. Information regarding the plutonium accounting for the two fires was declassified and released by the U.S. Department of Energy (DOE 1994), together with information on plant inventory differences at Rocky Flats and elsewhere.

The accountability data for the 1957 fire are discussed in detail in Appendix A. Overall accountability from before the fire to the completion of cleanup showed a decrease in book inventory of 6 kg of plutonium. However, an additional 2.3 kg of plutonium had been written off the inventory (declared lost). Thus, the total amount of plutonium that was unaccounted for was about 8.3 kg. This amount is much lower than one of the release estimates that had been made previously (Fairfield and Woods 1978). The cleanup following the fire was extended over a number of years. As a result it was not possible to identify amounts of solid waste that were removed from the fire area. The quantity Q_w in Equation (B-1) could not be estimated reliably from available data on solid wastes. Data from surveys of radioactive contamination were not found to support an estimate of the amount of residual contamination that was fixed in place by painting, Q_{rc} in Equation (B-1). Thus, although the inventory difference could be defined, there was inadequate information to estimate the amount of plutonium released.

Following the 1969 fire, more (104 kg) plutonium was recovered that had been in the plant inventory before the fire. Earlier inventory writeoffs had occurred because material could not be identified when periodic inventories were performed (just as the 2.3 kg of material had been written off the fire area inventory in 1957).

These results illustrate the difficulties associated with the use of accountability data to estimate releases. Finding more plutonium than was expected based upon the accounting system does not mean that there were no releases to the environment during the 1969 fire. Similarly, the reported inventory difference for the 1957 fire does not imply that the 8.3 kg of plutonium was released to the environment. The inventory difference does provide a gross upper bound that may be useful for some purposes.

The accountability data are not as reliable as expected, partly because plutonium is very difficult to measure. The measurement difficulties are illustrated in the following example of plutonium accountability for routine operation of a large facility.

B.3 EXAMPLE OF ACCOUNTABILITY DATA FOR ROUTINE OPERATIONS

To further evaluate the utility of the mass balance approach, routine operation of a plutonium processing facility was considered. Plutonium mass balance data for such a facility are estimated in this example. *The quantities received and shipped, the numbers of shipments, and the building inventory used in the discussion are not data from Rocky Flats but are speculative estimates of possible amounts*. Their basis is described next. Declassified information released by the U.S. Department of Energy (DOE 1994) shows that the Savannah River Site produced about 1500 kg of plutonium per year during the early 1960s. If Rocky Flats received that plutonium and a comparable amount from a combination of weapon returns and Hanford production, then the annual receipts would be 3000 kg. This corresponds to an average of 250 kg mo^{-1}, the rate used in this example. The number of shipments used in the example (11 mo^{-1}) is a guess. The amount per shipment (20 kg) was chosen to give a plant output (220 kg) that is comparable to the input.

Other quantities needed for the analysis are explicitly based upon published information for Rocky Flats. The estimated releases from the facility used in this example reflect the highest Building 71 releases that were measured during the 1960s. The atmospheric release estimates have been corrected for bias introduced by the sampling system and analytical procedure (Voillequé 1999).

For the example, the amounts of plutonium in wastes shipped to the Burial Ground at the National Reactor Testing Station (names used at the time) in Idaho and the numbers of barrels of waste generated per month are representative of estimates reported at that time. The estimated size of the inventory difference (ID) is also consistent with data from Rocky Flats operations. Annual inventory differences of 100 kg were common during the early 1960s and comparable quantities were used in the example. More details are given in Appendix A.

Assumptions and estimated quantities and the corresponding uncertainties in the main elements of the mass balance for the facility for an average month of operation are listed below.

Input: Monthly receipts of 250 kg of plutonium in 10 shipments of metal or other form having an average plutonium mass of 25 kg. The amount of plutonium in each of these shipments could be weighed to within 0.1 g.

Outputs: Monthly shipments of 220 kg of plutonium in 11 packages having an average plutonium mass of 20 kg. The mass of plutonium in each of these shipments could be weighed to within 0.1 g.

Measured losses consist of routine releases to the atmosphere and in liquid effluent discharges to Walnut Creek and shipments of solid wastes to Idaho.

(a) Release from the stack: a total of 1100 µCi of $^{239/240}$Pu in a month. This value, which exceeds the estimates for most years has been corrected for bias (Voillequé 1999). The estimated uncertainty range of 700–1600 µCi is based upon the same analysis.

(b) Releases in liquid discharges to Walnut Creek: a monthly total of 500 µCi of $^{239/240}$Pu. An estimated uncertainty range of 250–1000 µCi was chosen to reflect use of gross alpha counting and no information on the mixture of uranium and plutonium in the liquids discharged in the liquid waste stream, which also contained liquid from uranium processing in other buildings.

(c) Estimate of amount of plutonium in solid wastes shipped to Idaho: a monthly total of 2.5 kg in 300 barrels. The amount is more likely to be underestimated than overestimated because of difficulties in sampling discarded components and mixtures of solid materials. An uncertainty range of 1–9 kg is employed in the example. Current estimates of the plutonium in buried waste in Idaho are about 3 times greater than original estimates.

Building Inventory: At the end of the month an inventory of the facility identifies 18 kg of plutonium in components being fabricated and in identifiable scrap material. Although particular pieces can be weighed with the same precision identified above (±0.1 g), incomplete identification of scrap fines in process equipment leads to an estimated uncertainty in the inventory quantity of 0.1%.

Table B-1 summarizes the estimated quantities with uncertainty estimates based upon the assumptions given above. The uncertainties in the receipts (R) and shipments (S) reflect the total uncertainty for the month (that is, the combined uncertainties for the individual shipments). The example releases to air (A) and water (W) have been converted to mass, as shown. Estimates of uncertainties in these quantities were discussed above. Estimates of uncertainties in the amount of plutonium in shipments of solid wastes (SW) and in the monthly building inventory (BI) also correspond to the foregoing discussion.

Each of these elements of the mass balance is used in the calculation of inventory difference (ID) for the period. The equation used is

$$ID = R - S - (A + W + SW) - BI \qquad \text{(B-2)}$$

The uncertainty range for the inventory difference reflects the uncertainty ranges for all the quantities used in the calculation.

Some features of the tabulated estimates in the table deserve particular attention. First, the elements in the mass balance evaluation are not of commensurate magnitudes. The monthly receipts, shipments, and building inventory elements are much larger than the solid waste component, and the latter is very much larger than the highest measured monthly releases of plutonium to air and water. The largest uncertainties in plutonium mass are in those for the solid waste disposal and building inventory categories.

Table B-1. Example Mass Balance for Plutonium Processing Facility

Mass balance element	Measured mass (kg)	Uncertainty in mass (kg)
Pu received by facility (R)	250	± 3.2×10^{-4}
Pu sent from facility (S)	220	± 3.3×10^{-4}
Pu in releases to air (A)[a]	1.5×10^{-5}	$0.97–2.2 \times 10^{-5}$
Pu in releases to water (W)[a]	6.9×10^{-6}	$0.35–1.4 \times 10^{-5}$
Pu in solid wastes (SW)	2.5	1–9
Building Pu inventory (BI)	18	± 0.018
	Estimated[b] (kg)	
Inventory difference (ID)	9.5	3–11

[a] Estimates (µCi) were converted using a specific activity of 0.072 µCi µg^{-1}.
[b] Computed using Equation (B-2): ID = R – S – (A + W + SW) – BI.

The first feature is notable because of a previous review of the utility of the material balance approach. The National Academy of Science (NAS) conducted an independent review for the U.S. Environmental Protection Agency as part of the Superfund Amendments and Reauthorization Act of 1986. The NAS concluded that when there are major disparities in quantities processed and released, the engineering mass balance approach has no potential value in determining releases by difference (NAS 1990). The results in the table illustrate numerically the NAS conclusion for the semi-hypothetical Rocky Flats facility.

Because the quantities received and shipped could be determined with great precision, the uncertainties in R and S are small, about 1 part in 1 million in the example. Even so, these uncertainties alone are 20 and 40 times larger than estimated amounts of plutonium released to air and water, respectively. The ranges of these ratios are about 15–20 and 20–100, respectively. Overall uncertainties in the input and output quantities depend on the numbers of incoming and outgoing shipments. Assuming different numbers of packages would affect the uncertainties in R and S somewhat, but they would remain substantially greater than the ranges of releases to air and water.

The estimated uncertainty in the month-end building inventory of plutonium is less than 0.01% of the plutonium processing rate assumed for this example. However, that uncertainty of ~0.02 kg also greatly exceeds the highest recorded monthly discharges in gaseous and liquid wastes.

Uncertainties in the amount of plutonium in solid waste shipped offsite for burial are even larger and dominate the overall uncertainty of the inventory difference. These uncertainty estimates reflect the fact that for many years there was no reliable way to measure the amount of plutonium in waste shipments (more details are given in Appendix A). Even with contemporary equipment, measurements of plutonium in solid wastes are difficult and uncertain.

B.4 SUMMARY

Although it was initially expected that a mass balance approach would be useful in the evaluation of releases, this review showed that it is not feasible to make reliable quantitative estimates in this way. Because the post-fire cleanup work was extended over a period of years, it was not possible to identify waste shipments that were specifically related to the quantity Q_w in Equation (B-1). Further, before the 1970s, there were large uncertainties in solid waste measurements at Rocky Flats. This means if there were data that could be used to estimate the quantity Q_w, the result would be highly uncertain. Any estimate of Q_e based on Equation (B-1) would necessarily reflect the same large uncertainty.

During the early years of operation, there were also large uncertainties in inventory estimates because material was held up in processing areas. This was not be a major factor in an analysis of inventories before and after the 1957 fire because the development activities in Room 180 were relatively small in scale and had operated for only a few months. However, such uncertainties limit the reliability of mass balance accounting for other releases.

The uncertainties in solid waste discharges and in the amounts of material held up in processing equipment and lines are both much greater than airborne and liquid effluent releases. Although the measurements of receipts and shipments are quite precise, the uncertainties associated with these quantities are also substantially greater than routine releases to air and water. All the factors identified make mass balance accounting a very unreliable method for estimating such effluent releases. This conclusion is in agreement with a previous NAS report that assessed the same question for chemical processing facilities. The NAS found that when the amounts processed greatly exceeded the quantities released, the mass balance approach has no potential for determining the released amount by difference.

B.5 REFERENCES

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